SET – 16

Hydrogen atom – conserved quantities

(1) In terms of operators $\vec{p}$ and $\vec{r}$ we have

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{r}$$

(2) The equations of motion are.

$$\frac{d\vec{r}}{dt} = \frac{1}{i\hbar}[\vec{r}, H] = \frac{\partial H}{\partial \vec{p}} = \frac{\vec{p}}{\mu}$$

$$\frac{d\vec{p}}{dt} = \frac{1}{i\hbar}[\vec{p}, H] = -\frac{\partial H}{\partial \vec{r}} = -\frac{Ze^2\,\vec{r}}{r}$$

uses $[\vec{p}, \frac{1}{r}]$ which can be evaluated using $\vec{p} = \frac{\hbar}{i}\vec{\nabla}$

(3) The angular momentum is conserved because

$$\frac{d\vec{L}}{dt} = \frac{d}{dt}(\vec{r}\times\vec{p}) = \left(\frac{d\vec{r}}{dt}\right)\times\vec{p} + \vec{r}\times\left(\frac{d\vec{p}}{dt}\right)$$

$$= \frac{\vec{p}}{\mu}\times\vec{p} - \vec{r}\times\frac{Ze^2\,\vec{r}}{r}$$

$$= 0 \qquad \because [p_i, p_j] = 0 \text{ and } [r_i, r_j] = 0$$

More explicitly,

$$(\vec{p}\times\vec{p})_i = \epsilon_{ijk}\, p_j p_k$$

$$= \frac{1}{2}\epsilon_{ijk}\, p_j p_k + \frac{1}{2}\epsilon_{ijk}\, p_j p_k \qquad (\text{using } [p_j, p_k] = 0)$$

$$= \frac{1}{2}\epsilon_{ijk}\, p_j p_k + \frac{1}{2}\epsilon_{i\underset{k}{j}\underset{j}{k}}\, p_{\underset{j}{k}} p_{\underset{k}{j}}$$

$$= \frac{1}{2}(\epsilon_{ijk} + \epsilon_{ikj})\, p_k p_k$$

$$= 0.$$

4 Consider the axial vector, from classical hydrogen atom,

$$\vec{A} = \frac{\vec{r}}{r} - \frac{1}{\mu Z e^2} \vec{p} \times \vec{L} .$$

It is not Hermitian because

$$\vec{r}^\dagger = \vec{r}$$
$$\vec{p}^\dagger = \vec{p}$$
$$\vec{L}^\dagger = \vec{L} .$$

$$\begin{aligned}(\vec{p} \times \vec{L})^\dagger &= (\epsilon_{ijk} p_j L_k)^\dagger \\ &= \epsilon_{ijk} L_k^\dagger p_j^\dagger \\ &= \epsilon_{ijk} L_k p_j \\ &= -\vec{L} \times \vec{p}\end{aligned}$$

5 Thus, we construct

$$\vec{A} = \frac{\vec{r}}{r} - \frac{1}{\mu Z e^2} \frac{1}{2} (\vec{p} \times \vec{L} - \vec{L} \times \vec{p})$$

6 The measure of non-commutativity of the classical axial vector leads us to the following identity.

$$\begin{aligned}\vec{p} \times \vec{L} + \vec{L} \times \vec{p} &= \epsilon_{ijk} p_j L_k + \epsilon_{\substack{ijk \\ kj}} L_{\substack{j \\ k}} p_{\substack{k \\ j}} \\ &= \epsilon_{ijk} p_j L_k - \epsilon_{ijk} L_k p_j \\ &= \epsilon_{ijk} [p_j, L_k] \qquad \left(\text{using } \tfrac{1}{i\hbar}[\vec{p}, \delta\vec{\omega}\cdot\vec{L}] = \delta\vec{\omega} \times \vec{p}\right) \\ &= \epsilon_{ijk} \epsilon_{jkm} \, i\hbar \, p_m \qquad (\text{using } \epsilon_{ijk}\epsilon_{mjk} = 2\delta_{im}) \\ &= 2 \delta_{im} \, i\hbar \, p_m \\ &= 2 i\hbar \, \vec{p}\end{aligned}$$

⑦ Using ⑥ in ⑤ we can write the axial vector in the following form.

$$\vec{A} = \frac{\vec{r}}{r} - \frac{1}{\mu Z e^2}\frac{1}{2}\left(\vec{p}\times\vec{L} - \vec{L}\times\vec{p}\right)$$

$$= \frac{\vec{r}}{r} - \frac{1}{\mu Z e^2}\vec{p}\times\vec{L} + \frac{i\hbar}{\mu Z e^2}\vec{p}$$

$$= \frac{\vec{r}}{r} + \frac{1}{\mu Z e^2}\vec{L}\times\vec{p} - \frac{i\hbar}{\mu Z e^2}\vec{p}$$

⑧ Let us now verify that the Hermitian axial vector of ⑦ is indeed a constant of motion.

$$\frac{d\vec{A}}{dt} = \frac{d}{dt}\left[\frac{\vec{r}}{r} - \frac{1}{\mu Z e^2}\vec{p}\times\vec{L} + \frac{i\hbar}{\mu Z e^2}\vec{p}\right]$$

$$= \frac{d\vec{r}}{dt}\frac{1}{r} + \vec{r}\frac{d}{dt}\frac{1}{r} - \frac{1}{\mu Z e^2}\frac{d\vec{p}}{dt}\times\vec{L} - \frac{1}{\mu Z e^2}\vec{p}\times\underbrace{\frac{d\vec{L}}{dt}}_{=0} + \frac{i\hbar}{\mu Z e^2}\frac{d\vec{p}}{dt}$$

$$= \frac{\vec{p}}{\mu}\frac{1}{r} - \vec{r}\,\frac{\vec{p}}{\mu}\cdot\frac{\vec{r}}{r^3} + \frac{1}{\mu}\frac{\vec{r}}{r^3}\times\vec{L} - \frac{i\hbar}{\mu}\frac{\vec{r}}{r^3}$$

$$= \left[\vec{p}\,r^2 - \vec{r}\,\vec{p}\cdot\vec{r} + \frac{\vec{r}}{r^3}\times\vec{L}\,r^3 - i\hbar\vec{r}\right]\frac{1}{\mu r^3}$$

$$= \left[\vec{p}\,r^2 - \vec{r}\,\vec{p}\cdot\vec{r} + \vec{r}\times\vec{L} - i\hbar\vec{r}\right]\frac{1}{\mu r^3} \qquad \left(\left[\frac{1}{r}, \vec{L}\right] = 0 \text{ because } r \text{ is a scalar.}\right)$$

$$= \left[\vec{p}\,r^2 - \vec{r}\,\vec{p}\cdot\vec{r} + \vec{r}\times(\vec{r}\times\vec{p}) - i\hbar\vec{r}\right]\frac{1}{\mu r^3}$$

9 $\vec{r} \times (\vec{r} \times \vec{p}) = \epsilon_{ijk}\, r_j\, \epsilon_{kmn}\, r_m\, p_n$

$$= (\delta_{im}\delta_{jn} - \delta_{in}\delta_{jm})\, r_j\, r_m\, p_n$$

$$= r_j\, r_i\, p_j - r_j\, r_j\, p_i$$

$$= r_i\, r_j\, p_j - r_j\, r_j\, p_i$$

$$= \vec{r}\,(\vec{r}\cdot\vec{p}) - r^2\,\vec{p}$$

10 Using 9 in 8

$$\frac{d\vec{A}}{dt} = \left[\vec{p}\, r^2 - r^2\vec{p} + \vec{r}\,\vec{r}\cdot\vec{p} - \vec{r}\,\vec{p}\cdot\vec{r} - i\hbar\,\vec{r}\right]\frac{1}{\mu r^3}$$

11 $\vec{r}\,\vec{r}\cdot\vec{p} - \vec{r}\,\vec{p}\cdot\vec{r} = \vec{r}\,[r_j, p_j]$

$$= \vec{r}\, i\hbar\, \delta_{jj}$$

$$= 3 i\hbar\, \vec{r}$$

12 $\vec{p}\, r^2 - r^2\,\vec{p} = p_i\, r_j\, r_j - r_j\, r_j\, p_i$

$$= (r_j\, p_i - i\hbar\,\delta_{ji})\, r_j - r_j\, r_j\, p_i$$

$$= -i\hbar\, r_i + r_j\, p_i\, r_j - r_j\, r_j\, p_i$$

$$= -i\hbar\, r_i + r_j\,(r_j\, p_i - i\hbar\,\delta_{ij}) - r_j\, r_j\, p_i$$

$$= -2i\hbar\, r_i + r_j\, r_j\, p_i - r_j\, r_j\, p_i$$

$$= -2i\hbar\,\vec{r}$$

13 Using 11 and 12 in 10

$$\frac{d\vec{A}}{dt} = \left[-2i\hbar\,\vec{r} + 3i\hbar\,\vec{r} - i\hbar\,\vec{r} \right] \frac{1}{\mu r^3}$$

$$= 0.$$

Thus, $\vec{A}$ is a constant of motion.

14 To investigate the direction of $\vec{A}$ we calculate

$$\vec{A}\cdot\vec{L} = \left[\frac{\vec{r}}{r} - \frac{1}{\mu Z e^2}\,\vec{p}\times\vec{L} + \frac{i\hbar}{\mu Z e^2}\,\vec{p} \right]\cdot\vec{L}$$

$$= \frac{1}{r}\,\vec{r}\cdot(\vec{r}\times\vec{p}) - \frac{1}{\mu Z e^2}(\vec{p}\times\vec{L})\cdot\vec{L} + \frac{i\hbar}{\mu Z e^2}\,\vec{p}\cdot\vec{L}$$

$$= \frac{1}{r}\,\underbrace{(\vec{r}\times\vec{r})}_{=0}\cdot\vec{p} - \frac{1}{\mu Z e^2}\,\vec{p}\cdot(\vec{L}\times\vec{L}) + \frac{i\hbar}{\mu Z e^2}\,\vec{p}\cdot\vec{L}$$

$\because [r_i, r_j] = 0$

$$\vec{L}\times\vec{L} = i\hbar\,\vec{L} \qquad \left(\text{using } [L_i, L_j] = i\hbar\,\epsilon_{ijk} L_k\right)$$

Thus, we have.

$$\vec{A}\cdot\vec{L} = 0 - \frac{i\hbar}{\mu Z e^2}\,\vec{p}\cdot\vec{L} + \frac{i\hbar}{\mu Z e^2}\,\vec{p}\cdot\vec{L}$$

$$= 0.$$

Similarly (in homework) we see that $\vec{L}\cdot\vec{A} = 0.$

(15)
$$\vec{r}\cdot\vec{A} = \vec{r}\cdot\left[\frac{\vec{r}}{r} - \frac{1}{\mu Z e^2}\vec{p}\times\vec{L} + \frac{i\hbar}{\mu Z e^2}\vec{p}\right]$$
$$= r - \frac{1}{\mu Z e^2}\,\vec{r}\cdot(\vec{p}\times\vec{L}) + \frac{i\hbar}{\mu Z e^2}\,\vec{r}\cdot\vec{p}$$
$$= r - \frac{L^2}{\mu Z e^2} + \frac{i\hbar}{\mu Z e^2}\,\vec{r}\cdot\vec{p}$$

(16)
$$\vec{A}\cdot\vec{r} = \left[\frac{\vec{r}}{r} + \frac{1}{\mu Z e^2}\vec{L}\times\vec{p} - \frac{i\hbar}{\mu Z e^2}\vec{p}\right]\cdot\vec{r}$$
$$= r + \frac{1}{\mu Z e^2}\,\vec{L}\times\vec{p}\cdot\vec{r} - \frac{i\hbar}{\mu Z e^2}\,\vec{p}\cdot\vec{r}$$
$$= r - \frac{L^2}{\mu Z e^2} - \frac{i\hbar}{\mu Z e^2}\,\vec{p}\cdot\vec{r}$$

(17) Using (15) and (16)
$$\frac{1}{2}\left(\vec{r}\cdot\vec{A} + \vec{A}\cdot\vec{r}\right) = r - \frac{L^2}{\mu Z e^2} + \frac{i\hbar}{\mu Z e^2}\,\frac{1}{2}\left(\vec{r}\cdot\vec{p} - \vec{p}\cdot\vec{r}\right)$$
$$= r - \frac{L^2}{\mu Z e^2} + \frac{i\hbar}{\mu Z e^2}\,\frac{1}{2}\,3i\hbar$$
$$= r - \frac{L^2}{\mu Z e^2} - \frac{3\hbar^2}{2\mu Z e^2}$$

Observe that in the classical counter part $\vec{r}\cdot\vec{A} = rA\cos\theta$
led us to the motion to be elliptical, which is
obtained by setting $\hbar = 0$ here.

(18) Let us next evaluate the magnitude of the axial vector.

$$\vec{A}\cdot\vec{A} = \left[\frac{\vec{r}}{r} + \frac{1}{\mu Z e^2}\vec{L}\times\vec{p} - \frac{i\hbar}{\mu Z e^2}\vec{p}\right]\cdot\left[\frac{\vec{r}}{r} - \frac{1}{\mu Z e^2}\vec{p}\times\vec{L} + \frac{i\hbar}{\mu Z e^2}\vec{p}\right]$$

$$= 1 - \frac{1}{\mu Z e^2}\frac{\vec{r}}{r}\cdot\vec{p}\times\vec{L} + \frac{1}{\mu Z e^2}\vec{L}\times\vec{p}\cdot\frac{\vec{r}}{r}$$

$$+ \frac{i\hbar}{\mu Z e^2}\frac{\vec{r}}{r}\cdot\vec{p} - \frac{i\hbar}{\mu Z e^2}\vec{p}\cdot\frac{\vec{r}}{r} - \frac{1}{\mu^2 Z^2 e^4}(\vec{L}\times\vec{p})\cdot(\vec{p}\times\vec{L})$$

$$- \frac{i\hbar}{\mu^2 Z^2 e^4}\underbrace{\vec{L}\times\vec{p}\cdot\vec{p}}_{=0} + \frac{i\hbar}{\mu^2 Z^2 e^4}\underbrace{\vec{p}\cdot\vec{p}\times\vec{L}}_{=0} + \frac{\hbar^2}{\mu^2 Z^2 e^4}p^2$$

(19)
$$\vec{L}\times\vec{p}\cdot\frac{\vec{r}}{r} - \frac{\vec{r}}{r}\cdot\vec{p}\times\vec{L} = \vec{L}\cdot(\vec{p}\times\vec{r})\frac{1}{r} - \frac{1}{r}(\vec{r}\times\vec{p})\cdot\vec{L}$$

$$= -L^2\frac{1}{r} - \frac{1}{r}L^2$$

$$= -2\frac{L^2}{r} \qquad \left(\because [r,\vec{L}]=0,\ r \text{ being a scalar.}\right)$$

(20)
$$(\vec{L}\times\vec{p})\cdot(\vec{p}\times\vec{L}) = \epsilon_{ijk}L_j p_k\,\epsilon_{imn}p_m L_n$$

$$= (\delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km})L_j p_k p_m L_n$$

$$= L_j p_k p_j L_k - L_j p_k p_k L_j$$

$$= L_j p_k(L_k p_j + i\hbar\,\epsilon_{jkm}p_m) - \vec{L}\,p^2\cdot\vec{L} \qquad \left([\vec{p},\delta\vec{\omega}\cdot\vec{L}] = i\hbar\,\delta\vec{\omega}\times\vec{L}\right)$$

$$= L_j\underbrace{\vec{p}\cdot\vec{L}}_{=0}p_j + i\hbar\,\vec{L}\cdot\underbrace{(\vec{p}\times\vec{p})}_{=0} - p^2L^2 \qquad \left([p^2,\vec{L}]=0\right)$$

$\hookrightarrow$ scalar.

$$= -p^2L^2$$

$$\vec{p} = \frac{\hbar}{i}\vec{\nabla}$$

21 $$\frac{\vec{r}}{r}\cdot\vec{p} - \vec{p}\cdot\frac{\vec{r}}{r} = \frac{\vec{r}}{r}\cdot\frac{\hbar}{i}\vec{\nabla} - \frac{\hbar}{i}\vec{\nabla}\cdot\frac{\vec{r}}{r}$$

$$= -\frac{\hbar}{i}\left(\vec{\nabla}\cdot\frac{\vec{r}}{r}\right)$$

$$= -\frac{\hbar}{i}\left[\frac{3}{r} + \vec{r}\cdot\left(\vec{\nabla}\frac{1}{r}\right)\right]$$

$$= -\frac{\hbar}{i}\left[\frac{3}{r} - \frac{1}{r}\right]$$

$$= -\frac{2\hbar}{ir}$$

22 Using 19 to 21 in 18

$$\vec{A}\cdot\vec{A} = 1 - \frac{2}{\mu Z e^2}\frac{L^2}{r} - \frac{i\hbar}{\mu Z e^2}\frac{2\hbar}{ir} + \frac{p^2 L^2}{\mu^2 Z^2 e^4} + \frac{p^2\hbar^2}{\mu^2 Z^2 e^4}$$

$$= 1 - \frac{2}{\mu Z e^2}\frac{(L^2+\hbar^2)}{r} + \frac{p^2(L^2+\hbar^2)}{\mu^2 Z^2 e^4}$$

$$= 1 + \frac{2}{\mu Z^2 e^4}(L^2+\hbar^2)\left[\frac{p^2}{2\mu} - \frac{Ze^2}{r}\right]$$

$$= 1 + \frac{2}{\mu Z^2 e^4}(L^2+\hbar^2)\,H$$

23 Replacing $L = n\hbar$ $\quad n = 0, 1, 2, \ldots$

$$H = -\frac{\mu Z^2 e^4}{2\hbar^2}\frac{1}{n^2}(1 - A^2)$$

with $n = 1, 2, 3, \ldots$

(24) Summary :

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{r}$$

$$\frac{d\vec{r}}{dt} = \frac{1}{i\hbar}[\vec{r}, H] = \frac{\partial H}{\partial \vec{p}} = \frac{\vec{p}}{\mu}.$$

$$\frac{d\vec{p}}{dt} = \frac{1}{i\hbar}[\vec{p}, H] = -\frac{\partial H}{\partial \vec{r}} = -\frac{Ze^2\,\vec{r}}{r}$$

$$\vec{L} = \vec{r} \times \vec{p}$$

$$\frac{d\vec{L}}{dt} = 0$$

$$\vec{A} = \frac{\vec{r}}{r} - \frac{1}{\mu Ze^2}\vec{p} \times \vec{L} + \frac{i\hbar}{\mu Ze^2}\vec{p}$$

$$\vec{p} \times \vec{L} + \vec{L} \times \vec{p} = 2i\hbar\vec{p}$$

$$\frac{d\vec{A}}{dt} = 0$$

$$\vec{A} \cdot \vec{L} = \vec{L} \cdot \vec{A} = 0$$

$$\frac{1}{2}(\vec{A} \cdot \vec{r} + \vec{r} \cdot \vec{A}) = r - \frac{L^2}{\mu Ze^2} - \frac{3\hbar^2}{2\mu Ze^2}.$$

$$A^2 = 1 + \frac{2H(L^2 + \hbar^2)}{\mu Z^2 e^4}$$